

ACETYLATION OF STARCH WITH KETENE

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Various substances have been successfully acetylated with ketene, but, with the exception of several patents (1) the literature discloses few attempts to use it to acetylate carbohydrates. Van Alphen (2) was unsuccessful in his attempt to acetylate glucose and Hurd *et al.* (3) could not isolate glucose pentaacetate, although they did obtain partial acetylation of glucose and some of its derivatives. Vestling and Rebstock (4) by using ketene were able to prepare and isolate a monoacetylisopropylidenascorbic acid. We are aware of only one article dealing with the acetylation of starch with ketene (5). The maximum substitution reported in that article was 9.43% acetyl. The work reported here was undertaken to determine the conditions necessary for more complete acetylation of starch with ketene and to compare the products thus prepared with those acetylated with acetic anhydride.

Acetylation of starch without pretreatment of some kind leads to extensive degradation because of the drastic conditions necessary for the reaction. It has been claimed that nitromethane (6) is an effective pretreatment agent in the acetylation of cellulose, and pyridine (7) and formic acid (8) have been used as pretreatment agents for starch in acylation with acid anhydride. Nitromethane and pyridine were not satisfactory for use with ketene, partly because of side reactions. An extremely reactive starch, which will produce a rather homogeneous acetylated product, can be made with formic acid, but this reagent reacts with acetic anhydride (9) and with ketene (10). Acetic acid, which is an effective pretreatment agent in the acetylation with acetic anhydride (11) is equally effective when ketene is used. Water would be expected to give similar results, since ketene reacts with it to form acetic acid, but the reaction required more ketene, and the products seemed to be slightly inferior. No attempt was made to pretreat starch with alkali because the salts formed on addition of ketene cause it to polymerize rapidly.

Catalysts are required in acetylation with ketene as well as with acetic anhydride. Basic catalysts in general were unsatisfactory because they catalyzed the polymerization of ketene more than the acetylation of starch. Sodium acetate, for instance, resulted in a highly colored product with a low acetyl value. In addition, higher concentrations of this catalyst caused clogging of the plate through which the gases passed. Anhydrous pyridine acted in a similar manner, but when water was present somewhat better results were obtained. Zinc chloride produced little acetylation. As found by previous investigators, most effective catalysts were mineral acids. Sulfuric acid was used in most of our experiments; *p*-toluenesulfonic acid was likewise effective, although somewhat larger amounts were necessary. Perchloric and phosphoric acids as well as

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hydrochloric acid showed considerable catalytic effect, but the latter was too volatile to be satisfactory.

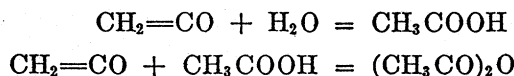
High temperatures were more satisfactory. Moderately high acetyl substitution could be obtained at 60°, but the products were only moderately soluble and gave grainy or incomplete solutions even when the viscosity was low. When attempts were made to increase the acetyl content by prolonging the treatment with ketene, discoloration took place, the reaction mixture turning dark brown when it became saturated with ketene. At 90°, however, the acetates produced were much more homogeneous, and only slight discoloration occurred. This result may explain in part why Burkhard and Degering (5) encountered color formation in their product, most of which was prepared at 25°, the maximum temperature reported being 56°. Moreover, their starch was apparently not pretreated and consequently had a lower reactivity.

The reaction medium should be a solvent for the product, otherwise the unreacted material will be coated by the product formed. Besides being a good pretreatment agent, acetic acid is a good solvent for starch acetate, although as will be pointed out later, it is not an inert medium. Of the more or less inert solvents, acetone and chloroform are effective for the lower range of temperatures. In the higher range, methyl ethyl ketone and tetrachloroethane are moderately effective. Acetone and other ketones, however, are not entirely inert solvents, since in the presence of acids they might react with ketene to form acetates of the enol form (12). Benzene and toluene are unsatisfactory because they separate the reaction mixture into two phases.

Best results were obtained when air-dry starch was pretreated with glacial acetic acid containing sulfuric acid as catalyst at 90°. The concentration of sulfuric acid must be adjusted carefully, because even a slight excess results in considerable degradation of the starch acetate and a slight deficiency results in a poorly acetylated product.

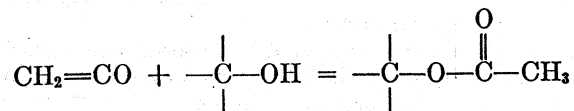
The acetylated product prepared with ketene under the best conditions compared favorably with a starch acetate prepared with acetic anhydride. The reference samples were made from air-dry starch pretreated with acetic acid containing sulfuric acid, followed by acetylation with acetic anhydride. Both materials were soluble in organic solvents like acetone, chloroform, ethylene chlorohydrin, and pyridine. They contained about 42% acetyl (theoretical 44.8%), and solutions made with them were of moderately high viscosity.

Rice and co-workers (13) have suggested that acetic anhydride might be an intermediate in the acetylation of carbohydrates with ketene. This suggestion is based on the well-known reactions of ketene with water and acetic acid:



Therefore, if acetylation is conducted in the presence of even traces of water or acetic acid, there is always the possibility that the actual acetylating agent is the acetic anhydride formed. As a matter of fact, ketene is a useful reagent for preparing acid anhydrides (14).

On the other hand, there is the other possibility of direct combination of the ketene with an alcoholic hydroxyl group to form the acetyl group:



The first possibility would be ruled out if water and acetic acid were completely eliminated from the reaction medium. In two recent papers describing the acetylation of isopropylidenascorbic acid (4) and ketones (15), anhydrous conditions of the reaction have been stressed. It will be shown in this paper that acetylation of anhydrous 1-butanol with ketene in the presence of fuming sulfuric acid proceeded smoothly and completely to its theoretical value. Morey (16) carried out similar experiments but it is not quite clear whether anhydrous conditions were maintained. Acetylation of anhydrous starch was less complete than the parallel acetylation with acetic anhydride (20% as against 44%). In the latter case, however, the acetylation medium, because of the formation of acetic acid during the reaction, was different from that used in ketene acetylation (tetrachloroethane). As a matter of fact, when tetrachloroethane was added to the acetic anhydride acetylation medium the rate of acetylation was retarded. These experiments indicate direct acetylation with ketene but do not furnish conclusive proof because even with minute traces of water continuous formation of acetic anhydride is possible.

EXPERIMENTAL

Acetic anhydride acetylation. Glacial acetic acid had no apparent effect on anhydrous starch (dried at 100°), but it had a marked effect on either air-dry starch or anhydrous starch which had been hydrated by exposure to the atmosphere. Good results have been obtained with starch of moisture contents ranging from 10% to 20%, although most of the samples had 10% to 13%. Small quantities of glacial acetic acid (about half the weight of starch) produced noticeable swelling. It could be noticed first at a temperature of 45° to 50°, and at 60° (the minimum temperature used in our work) the action apparently took place within a few minutes. For reaction, 25 ml. of glacial acetic acid containing 0.14 g. of concentrated sulfuric acid was added, with stirring, to 50 g. (dry basis) of air-dry white potato starch in a round-bottom flask in a heating-bath. After half an hour acetic anhydride was added, the total amount being slightly in excess of that theoretically required, allowing for the water present. At 90° or above, the starch reacted with the acetic anhydride almost instantaneously. At 60°, four to five hours was required. The result of the reaction was a rather viscous solution which contained a few small granules. The material was stirred several times with large proportions of fresh cold water, resulting in a white product. Batches of 1500 g. were prepared in the same manner except that the acetic anhydride had to be added gradually. Small batches at 60° and 95° gave products which had 43.2% and 43.6% acetyl and viscosities (2.5% solutions in pyridine) of 31.5 and 9.1 centistokes, respectively.

Ketene acetylation. The source of ketene was acetone pyrolyzed in the Williams and Hurd type lamp (17).² The rate of ketene output by this lamp varies rather widely with the fluctuation in voltage if some control is not used. At the laboratory outlets the difference has been as much as 10 volts. An increase of 10 volts was found to increase the ketene

² As suggested privately by one of the authors (J. W. W.), the filament of the lamp was prepared from a coil made from 400 cm. of wire stretched to 140 cm.

output four times within the ranges used. This fluctuation was considerably reduced by a constant-voltage transformer. Also, the filament itself seems to change with use, giving a reduced output of ketene for the same current.

The ketene acetylations were carried out in a bottle of about 350-ml. capacity fitted with a stirrer and a condenser. The gases from the ketene lamp were led into this bottle through a fritted-glass filter in the bottom. The best results were obtained in the following manner: Thirteen milliliters of glacial acetic acid containing 0.063 g. of concentrated sulfuric acid was stirred into 25 g. (dry basis) of air-dry white potato starch in a bottle, which was placed in a bath at 90°. The ketene lamp was started immediately, and half an hour later 37 ml. of glacial acetic acid was added. About an hour after this the starch began to go into solution. After 4.25 hours at an output of approximately 0.3 mole per hour, the ketene lamp was shut off. A sample of the product examined under the microscope showed few granules. Half an hour later the reaction mixture was stirred vigorously with cold water, separated, washed twice more with cold tap water, and then washed twice on the filter with distilled water. The oven-dried (100°) starch acetate (38.6 g.) had an acetyl value of 42.5% and a viscosity (2.5% in pyridine) of 6.5 centistokes.

Acetylation of 1-butanol. The butanol used (50 ml.) had been distilled from sodium through a fractionating column. The acetone used for preparing the ketene was A.C.S. reagent grade which had been dried over calcium chloride and then distilled from "Drierite" directly into the boiler of the ketene lamp. The butanol with two drops of fuming sulfuric acid as catalyst was added after dry air and then ketene had been run through the system. After the butanol had been saturated with ketene (about 1.75 hours), the reaction mixture became brown and had an ester-like odor. It was distilled under reduced pressure to remove dissolved ketene and then redistilled at atmospheric pressure through a fractionating column. All but 2 ml. of the material had the constant boiling point 125° (uncor.) and contained 36.9% acetyl (theoretical, 37.05%).

Acetylation of starch under anhydrous conditions. Fifty grams of starch (dry basis) was made into a paste with 100 ml. of distilled water on the steam-bath. The water was removed at room temperature by washing with alcohol and then ether. The resulting material was ground and divided into two portions, which were set aside in a vacuum desiccator over P_2O_5 at room temperature for more than a month, the P_2O_5 being changed several times. In the meantime, two 1-gram portions of *p*-toluenesulfonic acid monohydrate were dried under vacuum over $MgClO_4$ at 78°. After dry air was drawn through the system, one portion (A) of starch with one portion of *p*-toluenesulfonic acid and 50 ml. of dry redistilled tetrachloroethane was placed in the reaction flask. The other portion of starch (B) with the rest of *p*-toluenesulfonic acid and 50 ml. of dry redistilled tetrachloroethane was placed in a second flask fitted with a stirrer and drying tube, and 50 ml. of acetic anhydride was added. The ketene lamp was started, and the heating-bath was raised to 90°. Neither portion showed much signs of reacting during the first two hours, although portion A darkened considerably and became saturated with ketene. The rate of ketene input was decreased, but the mixture was kept saturated. Portion B was the first to show signs of reacting, but both had begun to go into solution at the end of three hours. After eight hours the heat and the ketene lamp were shut off, and the material was allowed to stand overnight. The next day the two batches were stirred several times with alcohol to remove the tetrachloroethane. The acetic anhydride product contained 44.2% acetyl; the ketene product contained only 22.6%.

In an earlier experiment of the same type, no tetrachloroethane was added to the mixture containing acetic anhydride, resulting in more rapid acetylation. The ketene sample reacted very much like the one just described. The corresponding acetyl values were 44.1% and 20.3%. Dilution with tetrachloroethane seemed to slow down the rate of reaction with acetic anhydride, but the final result was about the same.

The esters were analyzed for acetyl by the alcoholic alkali method (18) developed for cellulose.

Viscosity determinations were made on 2.5% solutions in pyridine in Fenske modified

Ostwald tubes according to the procedure of the American Society for Testing Materials. The average density of the solutions was 0.988 g./ml.

SUMMARY

Starch has been acetylated with ketene in acetic acid with sulfuric acid as catalyst. The products were similar to those obtained by acetylating acetic acid pretreated starch with acetic anhydride.

The question whether ketene combines directly with the alcoholic hydroxyl group or acts through the formation of acetic anhydride is discussed.

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